

Photoelectron branching ratios and asymmetry parameters for the two outermost molecular orbitals of hydrogen cyanide

D M P Holland[†], A C Parr[‡] and J L Dehmer[§]

[†] Institute of Physical Science and Technology, University of Maryland, College Park, MD 20742, USA

[‡] Synchrotron Ultraviolet Radiation Facility, National Bureau of Standards, Washington, DC 20234, USA

[§] Argonne National Laboratory, Argonne, IL 60439, USA

Received 19 July 1983, in final form 23 November 1983

Abstract. Triply differential photoelectron spectroscopy has been performed on hydrogen cyanide in the photon energy range 14.5 to 24 eV, using synchrotron radiation. Photoelectron branching ratios and asymmetry parameters are presented for the two outermost molecular orbitals. The vibrationally resolved branching ratio $X^2\Pi(v_3=1)/(v_3=0)$ exhibits strong non-Franck-Condon behaviour from threshold to approximately 19 eV. The results are discussed in relation to similar studies on the isoelectronic molecules, N_2 , CO and C_2H_2 . The evidence suggests that the prominent non-Franck-Condon feature observed in the $HCN^+ X^2\Pi$ channel may arise, at least in part, from a shape resonantly enhanced autoionising state converging to a higher ionisation potential.

1. Introduction

Triply differential photoelectron spectroscopy has been shown to be a useful method of studying the dynamics of molecular photoionisation. Indeed, the ability to perform vibrationally resolved studies with continuously tunable synchrotron radiation has permitted the systematic mapping of vibrational effects through regions containing autoionisation or shape resonant phenomena (for a recent review, see Dehmer *et al* 1983). Such experimental data have provided a stringent test of recent theoretical advances aimed towards a clearer understanding of resonant behaviour in simple molecules.

As background for the present study, we consider the closely related, isoelectronic series N_2 , CO and C_2H_2 . Early measurements of the photoelectron asymmetry parameter, β , by Carlson (1971) and Carlson and Jonas (1971) produced fragmentary evidence of non-Franck-Condon behaviour in the vibrational branching ratio of the $3\sigma_g$ channel in the $N_2^+ X^2\Sigma_g^+$ state. This result has since been understood successfully in terms of an $l=3$ dominated σ_u shape resonance at about 10 eV kinetic energy (Dehmer *et al* 1979); see also Lucchese and McKoy (1981). The original prediction was followed by vibrationally resolved branching ratio (West *et al* 1980) and angular distribution (Carlson *et al* 1980) measurements, which confirmed the basic shape resonance mechanism. Similar studies have been performed on the 5σ ionisation channel in CO (Stockbauer *et al* 1979, Cole *et al* 1980, Stephens *et al* 1981); however,

even for this closely related case, the situation becomes more complicated. A shape resonance mechanism, identical to that which works so well for N_2 , suffices to account qualitatively for the behaviour of the stronger $v = 0, 1$ vibrational channels; however, this picture appears to break down for the very weak vibrational channels. In the likewise isoelectronic case of C_2H_2 the picture becomes still more uncertain. Experimental investigations (Parr *et al* 1982, Keller *et al* 1982) observed strong non-Franck-Condon behaviour, but none attributable to shape resonance effects in the photon energy range studied (from threshold to 26 eV). It was suggested (Parr *et al* 1982) that autoionisation from two intense absorption features led to the observed non-Franck-Condon vibrational branching ratios and v -dependent asymmetry parameters. A recent theoretical calculation using a time-dependent local-density approximation (Levine and Soven 1983) has now clarified and extended this tentative interpretation, and, further, has semiquantitatively reproduced the observed variation of β in this spectral range.

As vibrationally resolved work on N_2 , CO and C_2H_2 has been successful in studying a most interesting evolution of resonant behaviour, it appeared worthwhile to perform a similar investigation on a further member, HCN, of the same isoelectronic series. In addition, HCN contains a $C\equiv N$ bond which may be expected to possess some of the characteristics of the nitrogen $N\equiv N$ bond and therefore, to some extent, exhibit some of the shape resonance effects which have already been mentioned. In fact, investigations have been carried out on three cyanides, C_2N_2 (Holland *et al* 1983b), CH_3CN (Holland *et al* 1983a), and HCN, all of which possess a $C\equiv N$, in order to study the effect of different chemical environments of the CN group.

Most relevant to the present study on hydrogen cyanide are related photoabsorption cross sections (Price and Walsh 1945, Herzberg and Innes 1957, Nagata *et al* 1981), photoionisation yield curves (Dibeler and Liston 1968, Berkowitz *et al* 1969), photoelectron spectroscopy at 21.2 eV (Baker and Turner 1968, Turner *et al* 1970, Frost *et al* 1973, Fridh and Åsbrink 1975, Kimura *et al* 1981), and 40.8 eV (Potts and Williams 1974, Fridh and Åsbrink 1975), and electron impact excitation and ionisation (Tam and Brion 1974, Fridh and Åsbrink 1975, Chutjian *et al* 1977, Åsbrink *et al* 1978, Hitchcock and Brion 1979). Theoretical calculations of the molecular orbital sequence, geometric structure and neutral excited-state energies have been performed by McLean (1962), Palke and Lipscomb (1966), Pan and Allen (1967), Thiel and Schweig (1972), Schwenzer *et al* (1974), Fridh and Åsbrink (1975), Hansoul *et al* (1978) and Schirmer *et al* (1978). The molecular orbital sequence of hydrogen cyanide in its molecular linear ground state may be given as

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4.$$

The experimental values (Fridh and Åsbrink 1975) for the two lowest vertical ionisation potentials are $(1\pi)^{-1} X^2\Pi = 13.607$ and $(5\sigma)^{-1} A^2\Sigma^+ = 14.011$ eV. The non-bonding 5σ molecular orbital is associated with the nitrogen atom lone pair electrons, while the outer 1π orbital is weakly bonding. The photoelectron spectroscopy study of HCN by Fridh and Åsbrink indicates that the ν_2 bending frequency is not very active. This suggests that both the ground state and the first excited state of HCN^+ are linear or nearly so. The next ionic state is the B state whose photoelectron band lies between 19.0 and 20.3 eV. The band has most frequently been regarded as being due to the removal of a 4σ electron, although this simple picture has been seriously questioned (Hansoul *et al* 1978). The exact onset of this band is not extremely well known, but Frost *et al* (1973) have given the ionisation potential as $B^2\Sigma^+ = 19.06 \pm 0.01$ eV. This

state is not studied directly here, but it is relevant as the next highest ionisation potential onto which autoionisation structure may converge. Fridh and Åsbrink have given the energy of the $\text{C}\equiv\text{N}$ stretching vibration, ν_3 , as 0.223 eV, that of the C–H stretch ν_1 , as 0.370 eV, and a value of between 0.040 and 0.050 eV for the bending vibration, ν_2 .

2. Experimental

The experiment was performed using a hemispherical electron analyser (Parr *et al* 1980) coupled to a high aperture 2 m normal incidence monochromator (Ederer *et al* 1980) at the National Bureau of Standards SURF II storage ring (Madden 1980). The experimental procedure has been described previously (Parr *et al* 1982). As the light from the monochromator was elliptically polarised, the differential cross section in the dipole approximation, assuming randomly oriented target molecules, and electron analysis in a plane perpendicular to the photon propagation direction, may be written in the form (Samson and Starace 1975)

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} \left[1 + \frac{1}{4}\beta(3P \cos 2\theta + 1) \right] \quad (1)$$

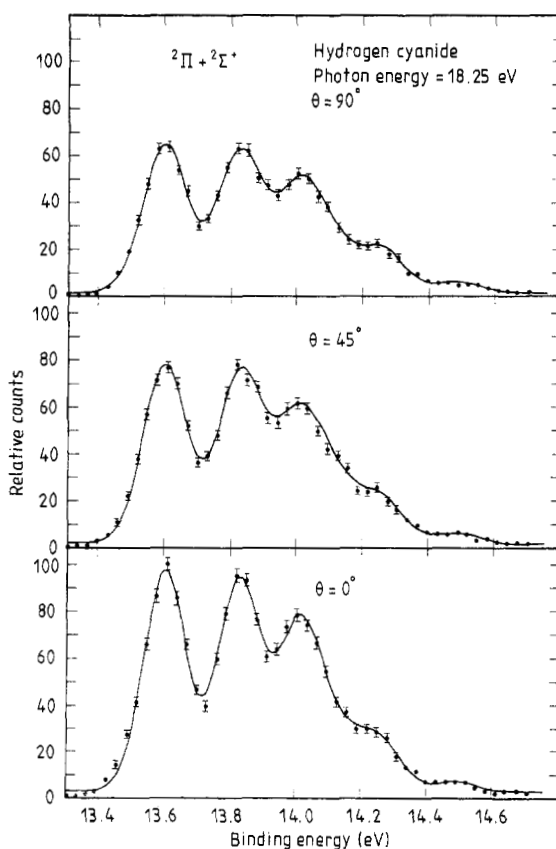


Figure 1. Photoelectron spectra of hydrogen cyanide at a photon energy of 18.25 eV and at $\theta = 0^\circ$, 45° and 90° . The spectra are normalised so that the maximum count in the $\theta = 0^\circ$ spectrum equals 100. The data points (●) and the nonlinear least-squares fit curve (—) are indicated.

where β is the photoelectron asymmetry parameter, θ is the photoelectron ejection angle relative to the major polarisation axis, and $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, the polarisation of the incoming light. At each photon energy reported here, photoelectron spectra encompassing the vibrational progressions of the $X^2\Pi$ and the $A^2\Sigma^+$ states were recorded at three angles of $\theta = 0^\circ$, 45° and 90° . A sample set of data at a photon energy of 18.25 eV is shown in figure 1, where the counts in the spectra have been normalised so that the maximum count in the $\theta = 0^\circ$ spectrum equals 100.

Owing to the complexity of the photoelectron spectrum, the instrumental resolution employed in the present study was insufficient to permit a reliable separation of all the vibrational structure. The small energy difference between the X and A state ionisation thresholds resulted in the high vibrational members of the X band overlapping the A band. A non-linear least-squares fit routine employing a Gaussian basis set and accurate electronic and vibrational energies (Fridh and Åsbrink 1975) failed to give reliable amplitudes for the weaker vibrational progressions. Hence, only the first two prominent peaks in the X band, which were well resolved, could be analysed by this method. The remainder of the spectrum, comprising the higher members of the X band and the entire A band, was treated as a whole. This procedure for analysing the data is discussed in greater detail in the following section. The errors shown on the data represent a combination of the uncertainty in the nonlinear least-squares fit, the degree of agreement between the parameters deduced from the redundant set of measurements at three angles and an estimate of possible systematic errors.

3. Results

Fridh and Åsbrink (1975) obtained a hydrogen cyanide photoelectron spectrum at 21.2 eV with a resolution of approximately 20 meV (FWHM). Examination of their spectrum revealed that in addition to the progression in ν_3 ($C\equiv N$ stretch), which dominated both the X and A state bands, structure could be discerned which was due to excitation of the ν_1 and ν_2 vibrational modes. At binding energies above 14.04 eV (the $A^2\Sigma^+$ threshold) the photoelectron spectrum became very complex. Below this energy, the spectrum was composed, basically, of two well separated peaks corresponding to the $\nu_3 = 0$ and 1 members of the X state progression. However, both of these peaks were supplemented by small admixtures of the bending mode ν_2 . Structure was observed for both $\nu_2 = 1$ and 2 and this resulted in the ν_3 progression having high energy shoulders. The resolution employed in the present experiment (120 meV) was insufficient to allow a reliable separation of the progressions in ν_2 and ν_3 . Hence, the data shown in figures 2 and 4 for the $\nu_3 = 0$ and 1 members of the $X^2\Pi$ ionic state may possess small admixtures of the ν_2 bending mode. Above 14.04 eV binding energy it was not feasible to disentangle the high lying vibrational members of the X state and the A state progressions. Hence, as mentioned earlier, only the first two peaks in the photoelectron spectra have been treated separately. The remainder, comprising the A state and the high vibrational members of the X state, has been treated as a single entity.

Figure 2 shows the spectral variation in the branching ratios among the three separate portions of the photoelectron spectrum discussed above. For photon energies above 19 eV, the ratios are approximately constant, within experimental uncertainty; however, below this energy considerable structure is observed. At the low energy limit of the present data the $\nu_3 = 0$ component of the ground ionic state, $X^2\Pi$, makes

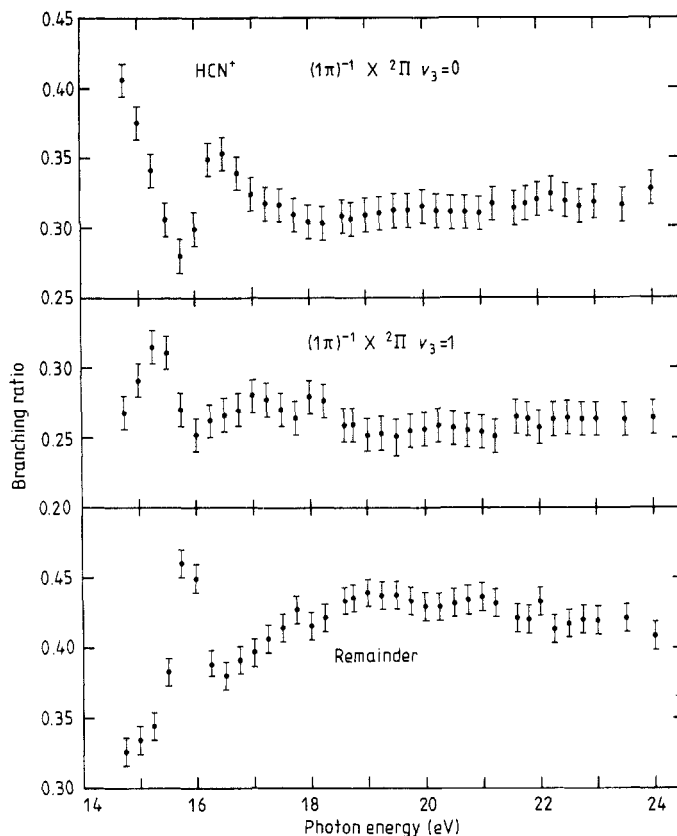


Figure 2. Photoelectron branching ratios for the $X^2\Pi v_3=0$ and 1 vibrational levels and the remainder, plotted as a function of photon energy.

the largest contribution. However, as the photon energy increases the $v_3=0$ contribution decreases, with a minimum at 15.75 eV, followed by a rise, peaking at 16.5 eV. In contrast, both the $v_3=1$ vibrational level and the remainder increase from their initial low values with the $v_3=1$ level peaking at 15.25 eV and the remainder at 15.75 eV. The branching ratio of $X^2\Pi (v_3=1)/(v_3=0)$ is displayed in figure 3 and the dramatic variations as a function of photon energy are immediately apparent. In addition to the peak centred around 15.5 eV, further oscillations can be seen at slightly higher energies, between 16.5 and 19.0 eV.

The asymmetry parameters for the various sections of the photoelectron spectrum are shown in figure 4. Figure 4(a) and (b) illustrates the variation in the $X^2\Pi v_3=0$ and 1 asymmetry parameters as a function of photon energy. Both β parameters exhibit a gradual rise as the photon energy increases, and above 19 eV, their magnitudes are very similar. This type of behaviour appears to be rather common among π orbitals of small molecules. Between 14 and 19 eV, however, there are noticeable differences in shape and magnitude between the two vibrational components. The asymmetry parameter for the remainder, figure 4(c), also shows some variations at low photon energies. As the photon energy increases the asymmetry parameter decreases from its value of about 0.4 at 14.75 eV and passes through a minimum at 15.75 eV. At higher photon energies its variation and magnitude are very similar to those shown

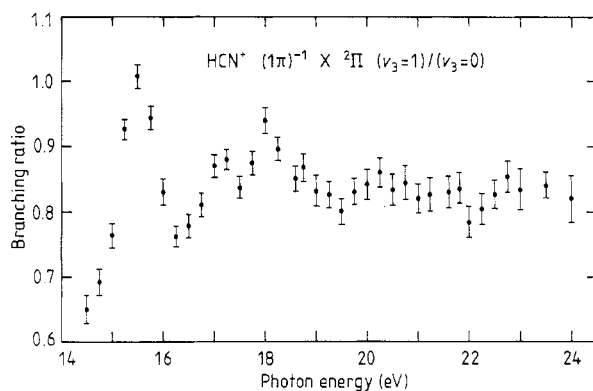


Figure 3. Vibrationally resolved branching ratio of $X^2\Pi (v_3=1)/(v_3=0)$ plotted as a function of photon energy.

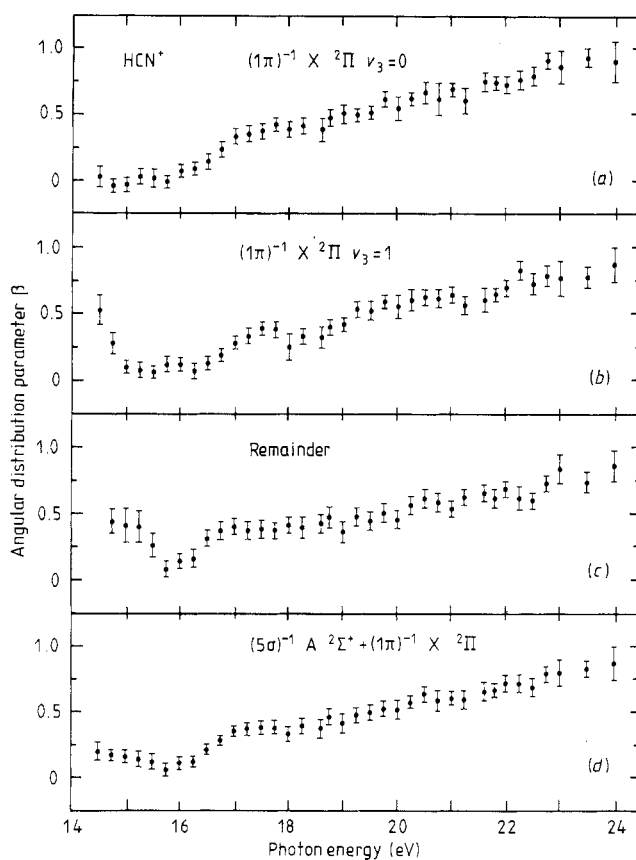


Figure 4. Photoelectron asymmetry parameters plotted as a function of photon energy. (a) $X^2\Pi v_3=0$, (b) $X^2\Pi v_3=1$, (c) remainder, (d) $(X^2\Pi + A^2\Sigma^+)$.

by the $X^2\Pi$ $v_3 = 0$ and 1 asymmetry parameters. In figure 4(d), the average asymmetry parameter for the $X^2\Pi$ plus the $A^2\Sigma^+$ states is plotted, that is, for the entire photoelectron spectrum observed in the present experiment. The variation as a function of photon energy is fairly smooth, and shows little evidence of the structure observable in the individual components contributing to this average β parameter. Nevertheless, this average ($^2\Pi + ^2\Sigma^+$) asymmetry parameter is included in the presentation of the experimental data for the sake of completeness and because it may prove useful as a test of future theoretical calculations.

The present experimental data on hydrogen cyanide can be divided into two categories. For photon energies greater than approximately 19 eV the branching ratios do not vary as a function of energy, and the $X^2\Pi$ $v_3 = 0$ and 1 asymmetry parameters exhibit similar behaviour. In contrast, below 19 eV, the vibrational branching ratios show non-Franck-Condon behaviour, especially apparent in the $X^2\Pi$ ($v_3 = 1$)/($v_3 = 0$) ratio, and the β parameters indicate vibrational state dependence. Such behaviour is indicative of resonant effects in the photoionisation process.

4. Discussion

The interpretation of the present branching ratios and asymmetry parameters of HCN naturally begins with consideration of the absorption features observed in the photoionisation yield curve of Dibeler and Liston (1968) and the electron impact energy-loss spectrum of Fridh and Åsbrink (1975). The Rydberg series converging onto the X and the A ionic states have been analysed, although not entirely consistently, by Tam and Brion (1974), Fridh and Åsbrink (1975) and Nagata *et al* (1981). However, all of these neutral states lie in an energy range below that in which the present data were taken. Immediately above the $X^2\Pi$ ionisation threshold (13.607 eV), the photoionisation spectrum shows some structure associated with vibrationally excited levels of the $X^2\Pi$ state, with superimposed features due to autoionising Rydberg levels in the region 13.84 to 14.01 eV. Since it is now known that the $A^2\Sigma^+$ threshold occurs at 14.011 eV it is reasonable to attribute much of this latter structure to autoionising transitions from Rydberg series converging onto the first excited state of the ion. Above this energy, the spectrum is dominated by an intense broad peak extending from approximately 14 to 19 eV, with the maximum around 15.5 eV. In the same energy region, Fridh and Åsbrink observed two peaks, each having a full width of approximately 2 eV, and assigned these to the transitions $4\sigma \rightarrow 2\pi$ (15.2 eV), and $4\sigma \rightarrow 3s\sigma$ (16.6 eV). (Rydberg structure converging onto the $(4\sigma)^{-1} B^2\Sigma^+$ state is apparently too weak to observe in these experiments). These strong absorption features, observable in the ionisation continua of both photon and electron impact measurements, suggest the presence of resonance phenomena. Hence it would appear worthwhile to consider the two most likely resonant mechanisms—shape and autoionising resonances—to ascertain whether either, or both, influence the photoionisation process in this region of the spectrum.

In regard to shape resonances, two aspects need to be considered: firstly, the possibility of shape resonance effects in the ionisation continuum, and secondly, their occurrence in the discrete part of the spectrum. In the analogous cases of photoionisation of the outer orbitals of N_2 and CO, theoretical work established the existence of a $\sigma(l=3)$ type shape resonance in the continuum (Dehmer *et al* 1983, and references therein). In predicting whether a resonance of a similar nature might be present in

hydrogen cyanide it is useful to examine the K-shell excitation spectrum. Hitchcock and Brion (1977, 1979, 1980) have recorded electron energy-loss spectra of C_2H_2 , HCN, N_2 and CO in the region of K-shell excitation. In comparing the nitrogen and hydrogen cyanide spectra it is noticeable that the two are very similar. Below their ionisation thresholds, both spectra are dominated by a single intense peak, followed by a small number of weak Rydberg peaks, and above threshold, a broad feature, with a width of many eV, can be observed. This would suggest that the additional H atom in HCN only causes a minor perturbation. The analysis and interpretation of the nitrogen K-shell spectrum in terms of shape resonance phenomena have been discussed by Dehmer and Dill (1976). It would appear that a generally similar interpretation could be applied to the K-shell spectrum of hydrogen cyanide. Dehmer and Dill attributed the broad peak occurring approximately 10 eV above threshold to a σ_u shape resonance in the continuum. A similar broad peak is observed in both the carbon and nitrogen K-shell excitation spectra of HCN approximately 14 to 15 eV above their respective ionisation potentials (Hitchcock and Brion 1979). Dehmer *et al* (1978) have identified this peak as being analogous to the nitrogen σ_u shape resonance. Shape resonance positions tend to shift approximately 1 to 3 eV higher in kinetic energy upon transferring from core spectra to valence-shell spectra. Therefore, it would appear that a σ -type resonance located on the $C\equiv N$ bond would not affect photoionisation in HCN until energies above those investigated in the present experiment. In this respect, the interpretation of the present data for HCN is similar to that for C_2N_2 (Holland *et al* 1983b). In C_2N_2 , however, a possibility existed of trapping on the C-C site, and some plausible evidence was cited to support this idea. In HCN this is not the case as the only alternative is a C-H site and hydrogen is not effective in producing shape resonant trapping in photoionisation. Furthermore, the cyanogen K-shell excitation spectra exhibited non-Rydberg type peaks which made plausible the suggestion of C-C trapping. In hydrogen cyanide this is not the case; fewer peaks are observed and these can be assigned to Rydberg transitions. Hence, these pieces of evidence tend to suggest that continuum shape resonance effects do not play a role in HCN photoionisation dynamics in the photon energy range under consideration.

Turning now to the possibility of shape resonance effects occurring below the ionisation onset, again, examination of the K-shell excitation spectrum provides the key to the problem. Below their respective thresholds, the K-shell excitation spectra of C_2H_2 , HCN, N_2 and CO are dominated by a single intense peak. In nitrogen, this strong feature has been identified as being due to the $1\sigma_u \rightarrow 1\pi_g$ transition. Dehmer and Dill (1976) have shown that this enhancement is a centrifugal barrier effect and is an example of a shape resonant phenomenon occurring in the discrete spectrum. Similar intense peaks located approximately 7 eV below the K-shell ionisation potentials in hydrogen cyanide have been assigned to the $1\sigma \rightarrow 2\pi$ transition (Hitchcock and Brion 1979). The energy positions of these intense K-shell features provide support for the assignment by Fridh and Åsbrink (1975) of the strong peak observed in the electron impact energy-loss spectrum as $4\sigma \rightarrow 2\pi$. By analogy to the isoelectronic molecules N_2 , CO and C_2H_2 , it would appear that both the $1\sigma \rightarrow 2\pi$, and the $4\sigma \rightarrow 2\pi$ transitions are shape resonantly enhanced in HCN.

Using this description of the HCN photoionisation dynamics, a picture emerges which is somewhat similar to that already encountered in C_2H_2 (Parr *et al* 1982). In the case of acetylene, two intense broad features dominated the photoionisation yield curves: the lower energy peak being assigned to the $2\sigma_u \rightarrow 1\pi_g$ transition, and the higher energy component to either $3\sigma \rightarrow 3\sigma_u$ or $3p\sigma_u$. Again, by analogy to K-shell

spectra, it was suggested that the $2\sigma_u \rightarrow 1\pi_g$ transition was shape resonantly enhanced (Parr *et al* 1982). Using the assignments of Fridh and Åsbrink (1975) and the evidence discussed above, the valence-shell spectrum of HCN may be described in the following manner. The peak with a maximum at 15.5 eV in the electron impact experiment, and 15.2 eV in the photoionisation measurement, can be regarded as a shape resonantly enhanced feature, and designated $4\sigma \rightarrow 2\pi$. This leaves the tentatively assigned $4\sigma \rightarrow 3s\sigma$ peak occurring around 16.6 eV as being non-resonantly enhanced.

From the analysis so far, it would appear that the non-Franck-Condon branching ratios observed in the present data might be explained in terms of autoionisation. It seems plausible to associate the peak in the $X^2\Pi (v_3=1)/(v_3=0)$ branching ratio around 15.5 eV with the $4\sigma \rightarrow 2\pi$ absorption feature. The intense peak observed by Dibeler and Liston extended to at least 19 eV, so it is conceivable that all the structure observed in the present data can be attributed to autoionisation from the shape resonantly enhanced $4\sigma \rightarrow 2\pi$ transition. However, this is doubtful since other states are known to exist between 16 and 19 eV. Although the peak centred around 16.6 eV was the weaker of the two observed by Fridh and Åsbrink, it appears with sufficient intensity to suggest that it should not be neglected. Furthermore, the intense absorption feature exhibited in the photoionisation yield curve has a highly asymmetric profile, with a high-energy shoulder which may have the same origin as the peak at 16.6 eV in the electron impact data. Hence, it is conceivable that autoionisation from this neutral excited state into the underlying continuum contributes to the fluctuations in the present data between 16 and 19 eV. Another possibility is that this high energy structure is associated with autoionisation from Rydberg levels converging onto the B state threshold at 19.06 eV. One must remember that even weak features in the total absorption cross section can produce significant structure in more sensitive dynamical parameters such as the vibrational branching ratios and β parameters.

In summary, the present data on HCN have been discussed within the context of similar studies on the isoelectronic molecules N_2 , CO and C_2H_2 . By examination of K-shell excitation spectra and structure observed in the present results, arguments have been proposed in support of a shape resonantly enhanced feature occurring around 15.5 eV. The isolated nature of this strong absorption feature, and the apparent absence of any superimposed sharp structure, would tend to suggest that a theoretical treatment could greatly clarify our understanding of this important extension of the N_2 , CO and C_2H_2 isoelectronic series.

Acknowledgments

We wish to thank R P Madden for his support and encouragement throughout this work. We appreciate the valuable assistance provided by G Rakowsky and the staff of the National Bureau of Standards' SURF II facility. This work was supported in part by the Office of Naval Research, the US Department of Energy and NATO Grant No 1939.

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